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Ship Materials Engineering Department  
Research & Development Report

Effect of Additives on the Morphology and Superconductivity of  $YBa_2Cu_3O_{6+x}$   
Ceramic Superconductors

by

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additions on grain size and superconducting performance were determined by microstructural examinations and measurements of electrical resistance versus temperature. Alumina was useful in constraining and reducing the grain size, but it adversely affected the superconducting transition temperature of the ceramic. This was attributed to the alumina removing oxygen from the superconductor. The oxygen loss causes the superconductor to transform from an orthorhombic crystal structure to a non-superconducting tetragonal phase. The silver oxide improved the superconducting transition temperature by several degrees even when as much as 25 weight percent. Deformation studies will now concentrate on this material.

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## ABSTRACT

Superplastic deformation is being studied as a means to turn the new ceramic superconductors into useful Naval hardware. Superplastic deformation can occur when a small grained material is subjected to stress at temperatures that are at least a half of their melting point. The ceramic superconductors, of which  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  is typical, require sintering treatments to create reasonably dense materials. However, sintering can result in a degree of grain growth that will not benefit superplastic deformation. To resolve the conflict of the need for full density with the need for a small grain size, the use of separate additives of  $\text{Al}_2\text{O}_3$  and  $\text{Ag}_2\text{O}$  particles to inhibit grain growth during sintering has been studied. The  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  starting ceramic powders were made by the calcining of  $\text{Y}_2\text{O}_3$ ,  $\text{CuO}$ , and  $\text{BaCO}_3$ .  $\text{Al}_2\text{O}_3$  and  $\text{Ag}_2\text{O}$  were added as powders to the ceramic in amounts of 1, 5, 10, and 15 weight percent and 5, 15, 20, and 30 weight percent, respectively. The effect of the additions on grain size and superconducting performance were determined by microstructural examinations and measurements of electrical resistance versus temperature. Alumina was useful in constraining and reducing the grain size, but it adversely affected the superconducting transition temperature of the ceramic. This was attributed to the alumina removing oxygen from the superconductor. The oxygen loss causes the superconductor to transform from an orthorhombic crystal structure to a non-superconducting tetragonal phase. The silver oxide improved the superconducting transition temperature by several degrees even when as much as 25 weight percent. Deformation studies will now concentrate on this material.

## ADMINISTRATIVE INFORMATION

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## INTRODUCTION

Existing electrical systems that use superconductors must be cooled with liquid helium. Ceramic superconductors have now been identified that can superconduct at liquid nitrogen temperatures (77K) and somewhat higher.<sup>(1)</sup> The ability to cool a superconductor with liquid nitrogen versus liquid helium has logistical advantages for the Navy in system reliability and supply. However, because of the brittle nature of ceramics, it has been difficult to process the new superconductors into useful forms, such as wires or microwave cavities. Superplastic deformation can be used to enhance the ease of fabrication of otherwise brittle ceramics and has been used with ceramics such as yttria stabilized zirconia.<sup>(2)</sup> Large deformations at relatively constant stress at high temperatures are the hallmark of superplastic deformation. This process can be used to make wires for magnets as used in electric drive system motors and generators. It can also be used to make shaped objects such as low loss microwave cavities or hollow tube "down-leads" that will transition the current leads from a room temperature world to that of a helium cooled superconducting storage magnet.

The key to achieving superplastic deformation is starting with and maintaining a small grain size (less than  $5 \times 10^{-6}$ m) in the material. Small grain size translates into a large proportion of grain boundaries and it is the grain boundaries which "slide" under stress at high temperatures and result in the superplastic deformations. Our goals with the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  ceramic superconductor are to determine a set of temperature, load and strain rate conditions that will result in superplastic deformation and to develop additives to maintain the small grain size in starting material during the various high temperature heat treatments that these materials must undergo before deformation.

#### EXPERIMENTAL PROCEDURE

The basic superconductor,  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ , was prepared by solid state reaction of commercial yttrium oxide and copper oxide with barium carbonate. The starting mixture was ball milled with distilled water as the dispersant and zirconia as the grinding media. After ball milling, the water was evaporated and the powder dried overnight at 110°C. The dry powder was calcined in air at 940°C for 6 hours and cooled very slowly to room temperature. Alumina powder (average size of  $10 \times 10^{-6}$ m) was then added in amounts of 1, 5, 10, and 15 wt % or silver oxide powder (average size of  $10 \times 10^{-6}$ m) was added in amounts

of 5, 15, 20, and 30 wt %. These mixtures, as well as the starting  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  powder with no alumina or silver oxide, were made into 1 cm discs and then heated to 920°C in air and held for 2 hours, cooled slowly in air to 600°C and held at that temperature for 6 hours in air before continuing a slow cool to room temperature.

The alumina was chosen as an additive as it is known to superplastically deform at 1000°C, which is close to the range of temperatures at which these materials might be deformed. The silver oxide,  $\text{Ag}_2\text{O}$ , was selected as it will decompose on heating to the sintering temperatures. The free silver will be plastic during deformation and may assist the onset of superplasticity. The free oxygen will be taken up by the frequently oxygen deficient  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  structure.

The particle size and surface area were determined by sedigraph and single point BET, respectively. The additive distributions in the matrix of  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  were examined using the scanning electron microprobe. The structural morphology of the samples was analyzed using the X-ray diffraction method. Indium solder was used to attached voltage and current leads to the specimens, so that the electrical resistance as a function of temperature could be measured by the four point method. The applied current was 10 milliamps. A nanovoltmeter with a sensitivity  $10^{-7}$  volts was used. To remove the effects of thermally induced voltages

from the resistance readings, the sign of the current was changed at each reading and the absolute value of the difference of the voltage readings was averaged and used in the plots of resistance versus temperature.

## RESULTS

### $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$

The as-synthesized (YBaCu) oxide powder had a density of 6.0 gm/cm<sup>3</sup> a surface area of 0.22 m<sup>2</sup>/gm. The density of as-synthesized powders is comparable to that reported in the literature<sup>(3)</sup>. The as-synthesized powder has a mean particle diameter of approximately 10 x 10<sup>-6</sup>m and, while it should be smaller for actual superplastic deformation, it is suitable for a study of the effect of additives on grain size control.

The morphology of the sintered  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  (123) superconducting disc, as was observed under an scanning electron microscope, is shown in Figure 1 and indicates that the as-synthesized 123 powders had sintered into elongated rods. The x-ray diffraction pattern obtained from the same sample is also shown in Figure 1 and indicates that the crystal structure of these sintered rods is similar to that of orthorhombic 123 materials as were reported in the literature<sup>(4)</sup>.

## ALUMINA ADDITIONS

The morphology of sintered 123 ceramic materials containing 0 to 15 wt. % alumina, as was observed under an electron probe, is shown in Figure 2 along with the elemental mappings the aluminum distribution. The aluminum from the additive ( $Al_2O_3$ ) is uniformly distributed throughout the matrix material (i.e. the 123 ceramic material). The addition of even 1 wt. % of  $Al_2O_3$  has a significant effect on the shape and topography of the  $YBa_2Cu_3O_{6+\delta}$  particles. Although our present experimental results do not suggest indicate the additive has suppressed or inhibited the grain growth of the 123 material during sintering or chemically eroded the surface in order to reduce the ultimate grain size of the matrix, the particle size appears to decrease with an increase in the concentration of added  $Al_2O_3$ .

In order to derive some semi-quantitative correlations between the (YBaCu) oxide grain size and the additive ( $Al_2O_3$ ), we have polished some sintered discs and obtained a number of micrographs at random areas that represent the surface of the sintered test sample. A typical example of such micrographs obtained from 0, 1, 5 and 15 wt. % alumina is shown in Figure 3. The gray area of the sample was later identified and was found to be orthorhombic phase of 123 material (the crystal phase of the dark areas of the 123 grains is predominantly

tetragonal phase). Figure 3 shows the grain size distribution of sintered 123 ceramic as a function of added alumina concentration. These results show that the as-synthesized 123 material has a very broad size distribution with an average grain size of approximately  $40 \times 10^{-6} \text{m}$  (max. and min. size values of approximately 60 and  $20 \times 10^{-6} \text{m}$ , respectively). The results indicate that as the concentration of alumina in the  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  matrix increases, the average grain size of superconducting 123 material and the broadness in the size distribution decreases. For example, the maximum, minimum and average grain size of 123 in sintered 15 wt. %  $\text{Al}_2\text{O}_3$  /  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  composites are approximately 5, 0.5 and 2 microns respectively.

The structure of all 123 samples containing alumina was determined using the wide angle x-ray diffraction method. Figure 5 shows a typical example of the type of x-ray diffractograms that were obtained from the additive / 123 composites. Although the x-ray results shown in Figure 5 at the first glance can only suggest that the intensity of the alumina peaks increases with an increase in the concentration of alumina, we found that a careful examination of such x-ray patterns can reveal important information regarding the effect of alumina on the crystal structure of 123 material. Figure 6 shows the results obtained from such an analysis. The results suggest that the superconducting orthorhombic phase of the 123 material decreases with an increasing alumina content and that the tetragonal phase of the 123 material increases with the addition of alumina.

The electrical resistivity of all samples (with and without the additive) is shown in Figure 7. The results suggest that the superconducting transition temperature ( $T_c$ ) of our samples decrease very sharply with an increase in the additive concentration. Once a critical  $T_c$  value (approximately 50 K) is reached, it appears that the effect of the addition of alumina (within the concentration range investigated) on  $T_c$  is not significant. The results also suggest that the normal state resistivity of alumina / 123 composites increases with an increase in the additive concentration. For example, the normal state resistivity of pure 123 and 1 wt. %  $\text{Al}_2\text{O}_3 \cdot 123$  composite measured at 100 K are approximately 6.5 and 8.5 milli ohm · cm respectively.

#### SILVER OXIDE ADDITIONS

The superconducting transition temperature,  $T_c$ , of the  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  increases from a range of 88 to 90 K without the silver oxide additions to a range of 92 to 93 K with the additions as measured by four point resistance (Figures 8). AC susceptibility measurements (to be fully reported elsewhere<sup>(5)</sup>) indicate that this increase can be as high as 97 K. The processing details to arrive at this improvement are the subject of a Navy patent disclosure<sup>(6)</sup>. The enhanced quality of the  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  with silver is further indicated by the resistivity values at the onset of the superconducting

transition, which are in range of 50 to 70 milliohm-cm for the  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  without silver versus 1.6 to 8 milliohm-cm with silver. Other researchers have reported similar improvements in the quality of  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  when adding silver<sup>(7)</sup>.

Microstructural examinations (Figures 9) show that the  $\text{Ag}_2\text{O}$  additions cause the 123 crystals to line up and orient themselves towards pores. This is in part responsible for the increase in  $T_c$  with silver additions. The  $\text{Ag}_2\text{O}$  decomposes above 230°C and upon calcining or sintering above this temperature the silver flows and accumulates at any pores. This would serve to orient the 123 crystals. This flow is good for improving the density and could prove useful in orienting the 123 during superplastic deformation. Oriented 123 can have enhanced current carrying capability, which would be of significant benefit. While the silver may improve the density of the sintered 123, it does not reduce the particle size. However, it may prevent excessive grain growth during sintering, a point which is currently being investigated.

## DISCUSSION

In general for the superplastic deformation of ceramic materials, the important requirements are (1) a very small particle or

grain size, and (2) the retention of the original crystal structure after deformation. However, the superconducting ceramic materials have to satisfy two additional requirements for namely, (3) the superconducting transition temperature and (4) the critical current have to be unaffected or even enhanced by the deformation process. Although, we have reported<sup>(8)</sup> that the chemical processing of (YBaCu) oxide can produce such ceramics to satisfy the first three requirements, the fine particle synthesis process is very time consuming. The present approach based on the additive induced grain growth inhibition during solid state reaction appears to have a better engineering applicability. The results obtained from the present investigation suggests that although, the selected additive (alumina) can fulfill the first requirement for superplastic deformation, it has degraded both the superconducting transition temperature and altered the crystal structure of the superconducting ceramic. However, the results of this investigation have provided important information that has to be considered for the selection of another suitable additive.

It has been reported in the literature<sup>(9)</sup> that the lower stoichiometric (YBaCu) oxides have both tetragonal crystal phase and low  $T_c$ . Therefore it is possible that the oxygen ions from the original (YBaCu) oxide lattice have been transferred to the matrix of the alumina. In all our 123 superconducting ceramic samples containing alumina, we always noticed that the morphology of 123 grains has lost its original smooth surface texture. The surface topography, on the

other hand represented that of an eroded or etched rod or plate surface (Figure 2). Since, such surface features can not be explained in terms of the sintering parameters, it is reasonable to attribute the differences to some chemical reaction process that may be occurring simultaneously during the sintering of  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  in  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}/\text{Al}_2\text{O}_3$  composites. We have not independently analyzed the chemical composition of either our superconducting ceramic powder or the commercial alumina powder. However, we have examined all samples under a polarized optical microscope using a standard colorization technique for identification of superconducting and non-superconducting phases in materials, that has been developed and routinely used at the Naval Research Laboratory, Washington, DC. All our samples showed mostly the superconducting crystalline phase in the pure material with heavy twinning of the grains. However, the samples containing the additive revealed that the orthorhombic grains that were surrounded by a large number of alumina particles, have transformed into the tetragonal phase. (The original twins were also discernible in those tetragonal grains.) From the colorization analysis it was thought that if the (YBaCu) oxide phase transformation is associated with the oxygen ion transfer to the vicinity of the aluminum ions, annealing of the low  $T_c$  samples in excess oxygen should increase the  $T_c$ , while a removal of the oxygen should further lower the  $T_c$ . Similarly, the orthorhombic phase of the low  $T_c$  samples, when annealed in excess oxygen should improve the orthorhombic phase content at the expense of the tetragonal phase and vice versa.

In order to test whether the superconducting transition temperature and structure are additive dependent or depend upon the chemical reactivity of the constituents (i.e. the ions) of the additive, additional experiments were carried out. In the first set of experiments, the 123 samples containing 0, 5 and 10 wt. % additive were annealed in excess flow of oxygen for 12 hours and in the second set of experiments, the  $\text{Al}_2\text{O}_3$  / 123 composites were annealed for 12 hours in continuously flowing air. The results of the above two sets of experiments is shown in Figure 10. The results suggest that the addition of oxygen to 5 and 10 wt. %  $\text{Al}_2\text{O}_3$  / 123 composites has increased the  $T_c$ . A similar increase (although not shown in Figure 9) but to a lesser extent was noticed in the orthorhombic crystalline structure of these samples. Annealing in excess air flow to a lesser extent has decreased the  $T_c$ . However, a reasonable increase in the tetragonal phase was observed for these samples.

It has to be emphasized that although (at the present time) the mechanism of the phase transformation in (YBaCu) oxide ceramic due to the addition of alumina is very qualitative, we intend to analyze all our samples for the true chemical composition in order to unequivocally determine the sequence of events of the chemical reaction process involved during the sintering of  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  in presence of alumina as an additive.

The  $\text{Ag}_2\text{O}$  additions have improved the  $T_c$ . Silver oxide breakdown on heating the composites has two beneficial effects. First, as the composite is heated to the calcining or sintering temperatures the silver becomes very mobile and easily migrates to and fills voids in the structure. This not only improves density and mechanical integrity but it also serves to align the 123 grains. This leads to higher  $T_c$  and current carrying capability. Second the oxygen from the silver oxide is free to diffuse into the 123 lattice which is generally oxygen deficient.

Deformation studies with 123 will concentrate on the silver additions. Although it doesn't reduce grain size like alumina does, it does improve  $T_c$  and density, and if the starting powder is small enough the mobility of silver at high temperatures may enhance the onset of superplastic deformation.

## CONCLUSIONS

From the present investigation the following conclusions are made:

1. Sintered  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  superconducting ceramics with small grains can be produced by the solid state reaction method with the addition of alumina as an additive.
2. The reduction of the sintered  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  grain size increases with an increase in the alumina additive concentration.
3. The addition of alumina to the  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  not only lowers the superconducting transition temperature ( $T_c$ ) of the sintered composite, but also alters the  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  crystal structure (the orthorhombic phase decreases while the additive tends to stabilize the tetragonal phase).
4. Reannealing in excess oxygen for 12 hours shows an improvement in the  $T_c$  of the  $(\text{YBaCu})$  oxide/ $\text{Al}_2\text{O}_3$  composites. However, annealing in excess air flow for 12 hours tend to lower the  $T_c$  slightly.
5. Adding silver oxide to  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  results in increasing the  $T_c$  from a range of 88 to 90 K to one of 92 to 93 K.

6. Silver oxide additions result in the  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  crystals lining up at voids in the structure. This alignment may prove useful in promoting superplastic deformation and enhancing current carrying capability.

#### ACKNOWLEDGMENTS

The authors wish to acknowledge Drs. Syed Qadri and Chandra Pande of the Naval Research Laboratory for producing the X-ray diffraction patterns and for using the colorization technique for phase identification.



Fig. 1a. SEM micrograph.

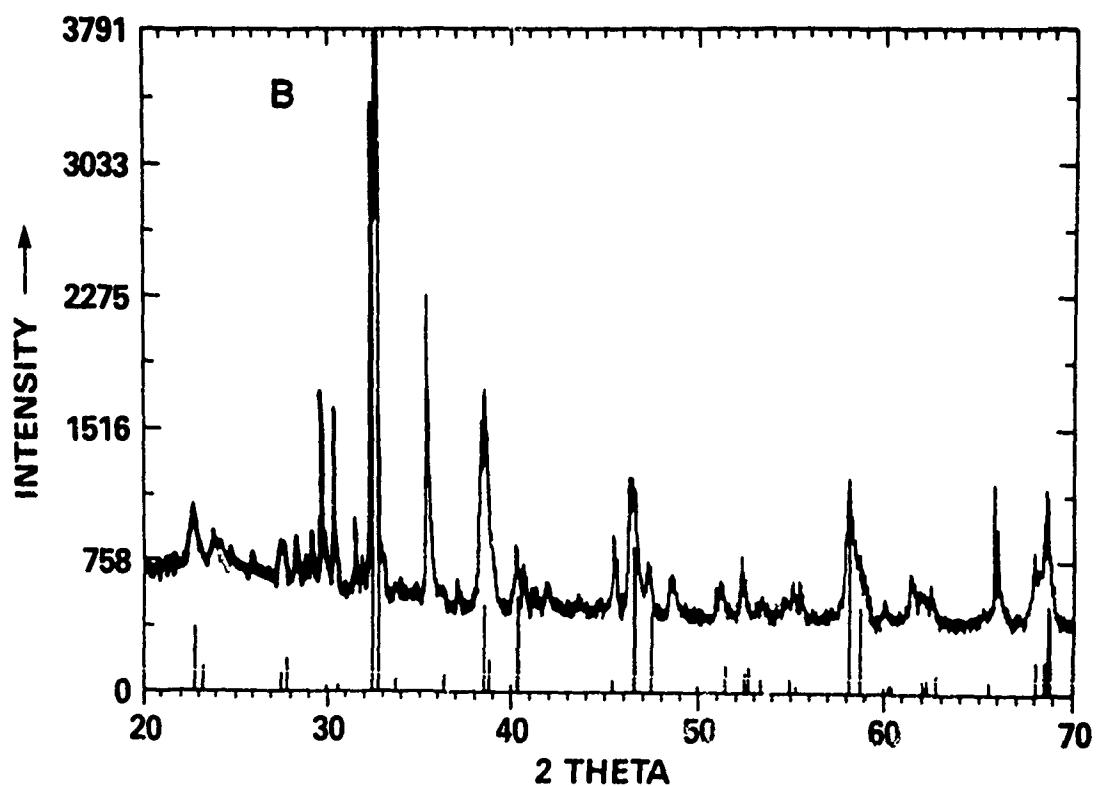
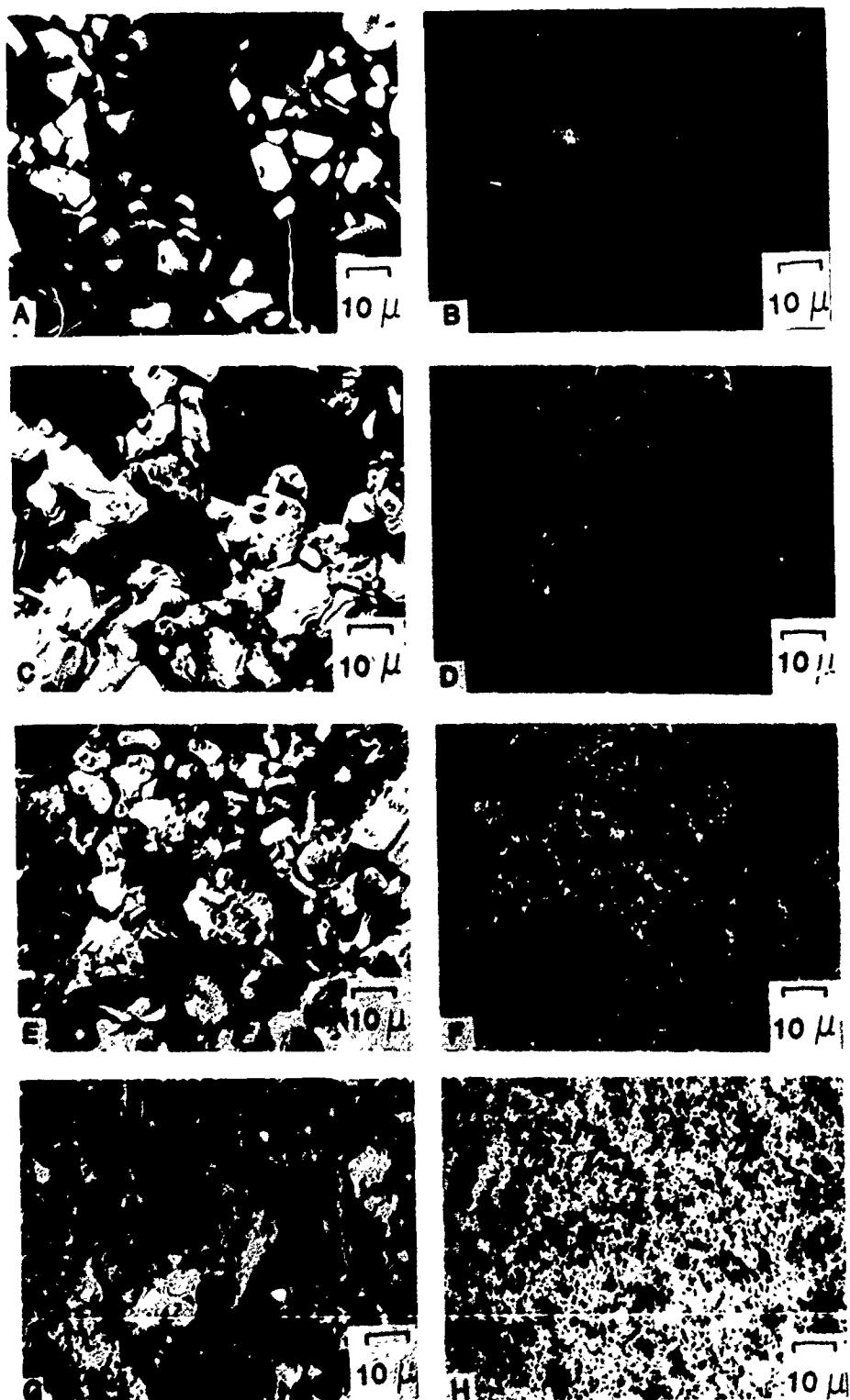
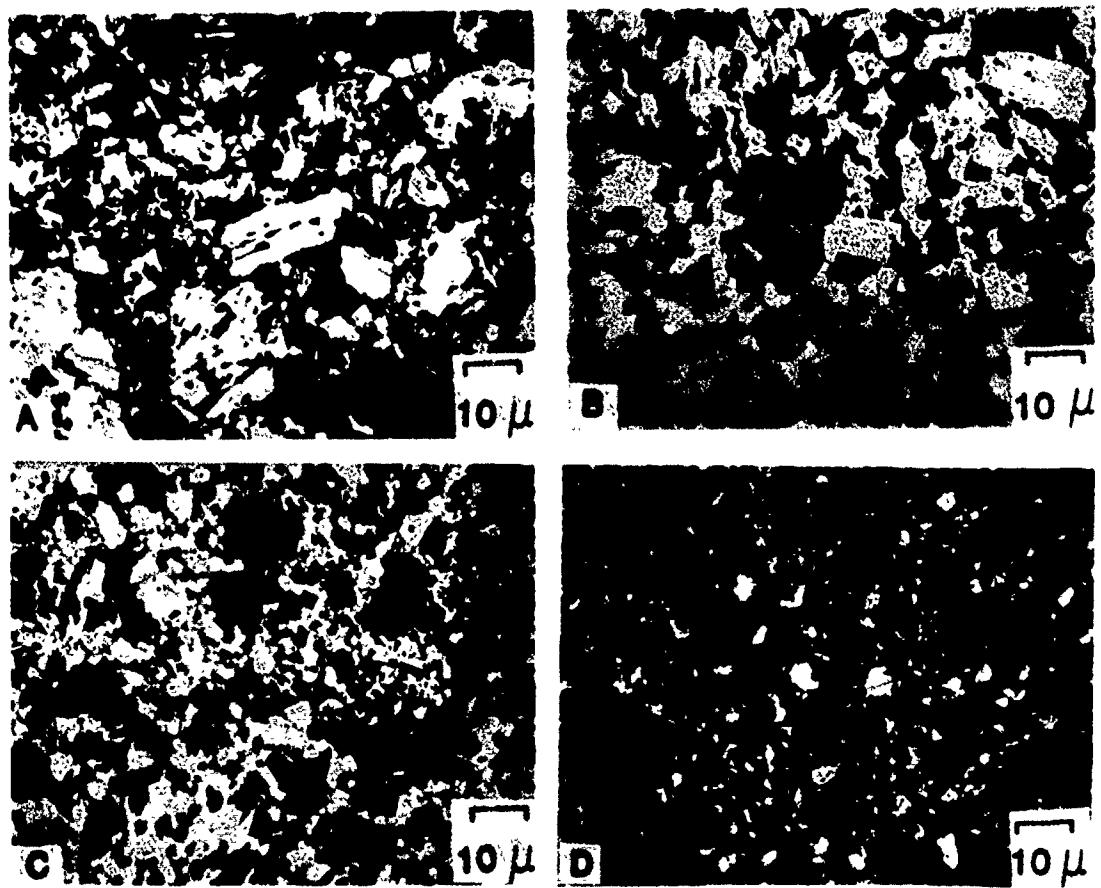


Fig. 1b. XRD pattern.

Fig. 1. As-synthesized pure superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  SEM morphology and XRD pattern.



**Fig. 2.** Back scattered electron images and the corresponding aluminum X-ray scan images of as-sintered alumina/(YBaCu) oxide composites. Concentration of alumina in the composites are (A,B) 0, (C,D) 1, (E,F) 5 and (G,H) 15 weight percent.



**Fig. 3.** Optical micrographs of sintered polished alumina/(YBaCu) oxide composites containing (A) 0, (B) 1, (C) 5 and (D) 15 weight percent alumina.

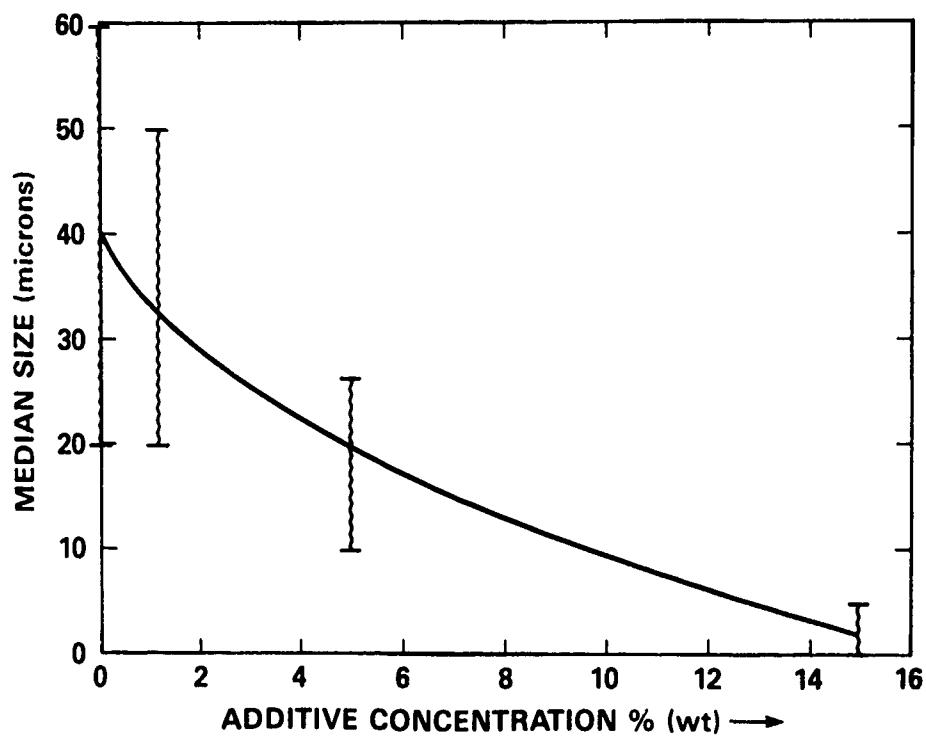


Fig. 4. Grain size distribution of superconducting yttrium, barium, and copper oxide ceramic as a function of additive concentration.

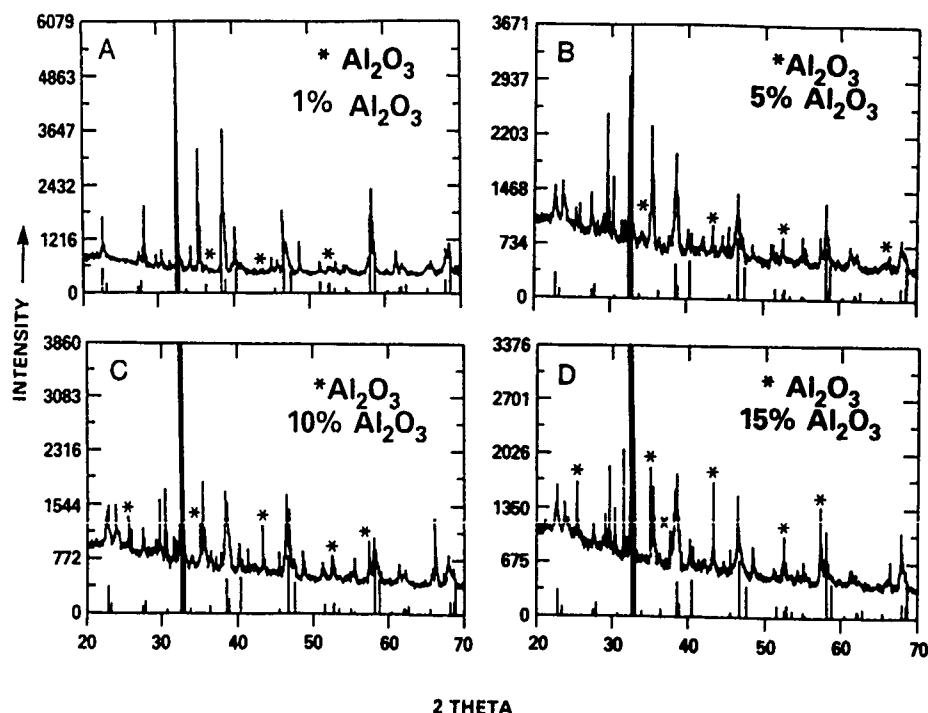


Fig. 5. Wide angle X-ray diffraction patterns of alumina/(YBaCu) oxide composites.

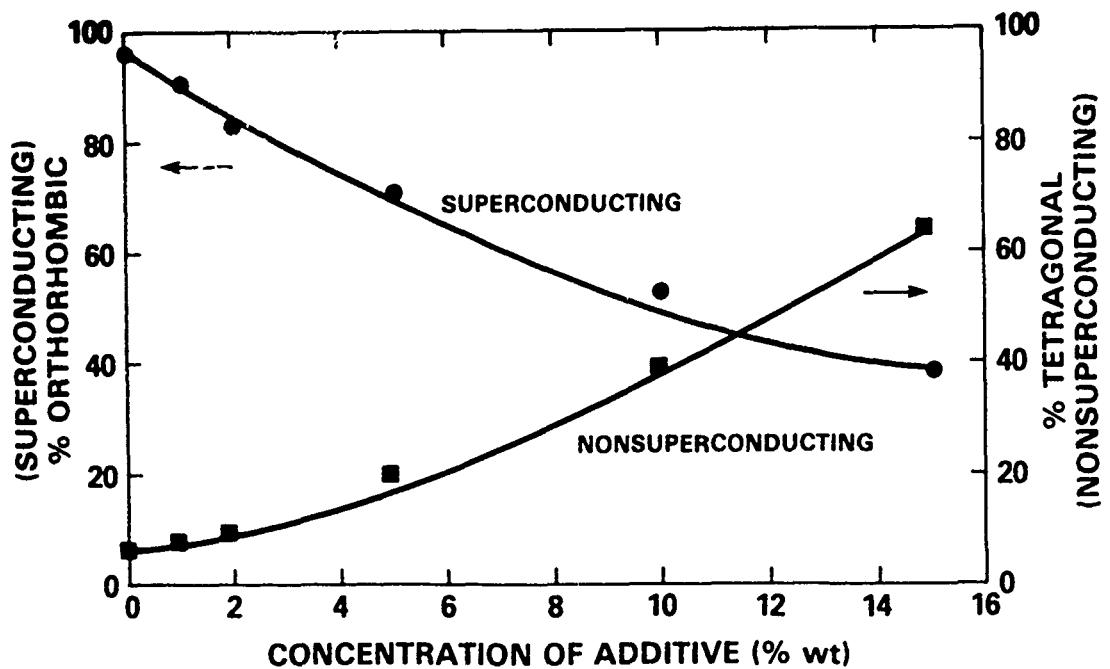


Fig. 6. Percent orthorhombic and percent tetragonal crystal phase versus the additive concentration of alumina/(YBaCu) oxide composites.

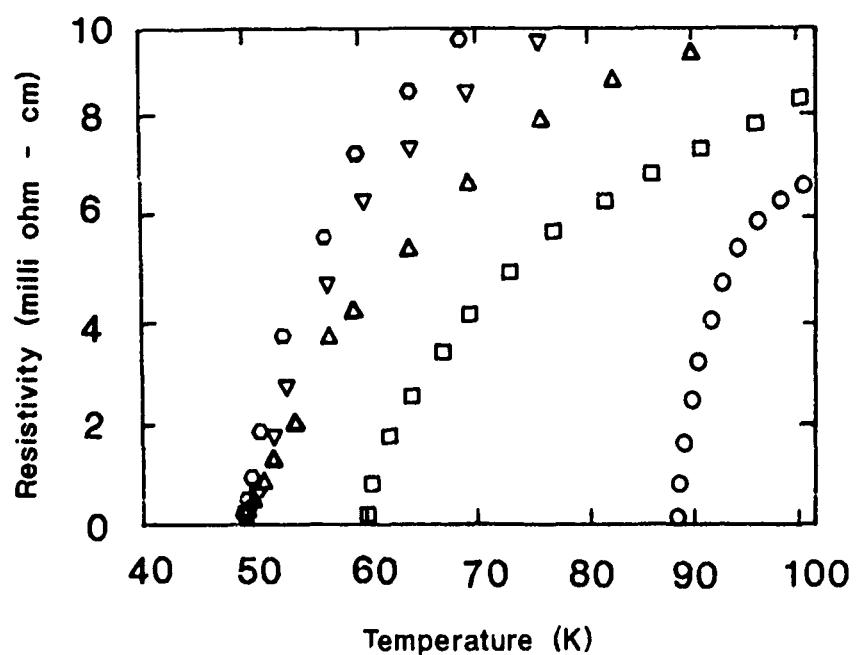


Fig. 7. Electrical resistivity of sintered  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}/\text{Al}_2\text{O}_3$  composites. Alumina concentration (○) 0, (□) 1, (△) 2, (▽) 5 and (○) 10 weight percent.

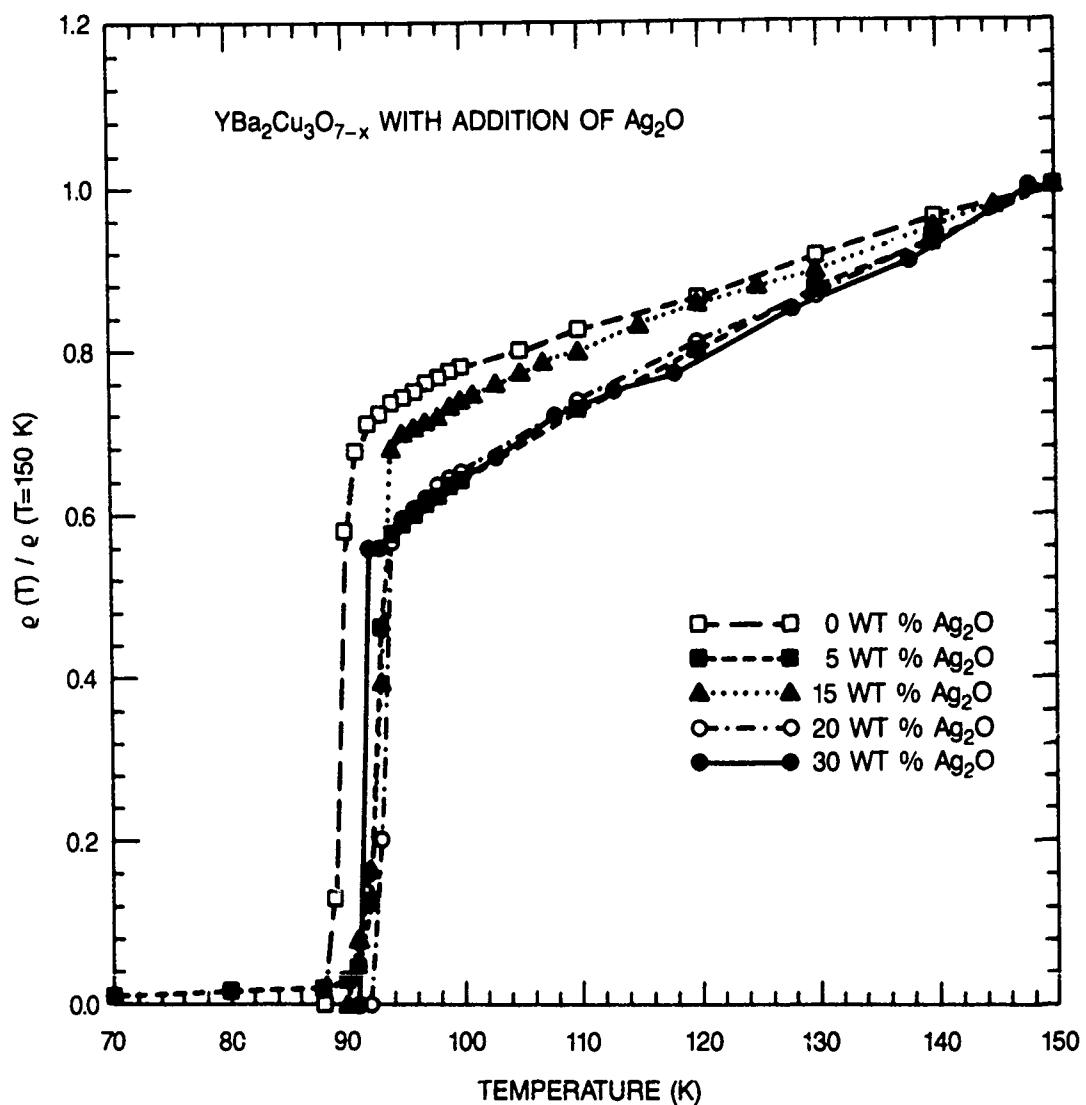


Fig. 8. Normalized resistivity of  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  with silver oxide additions.

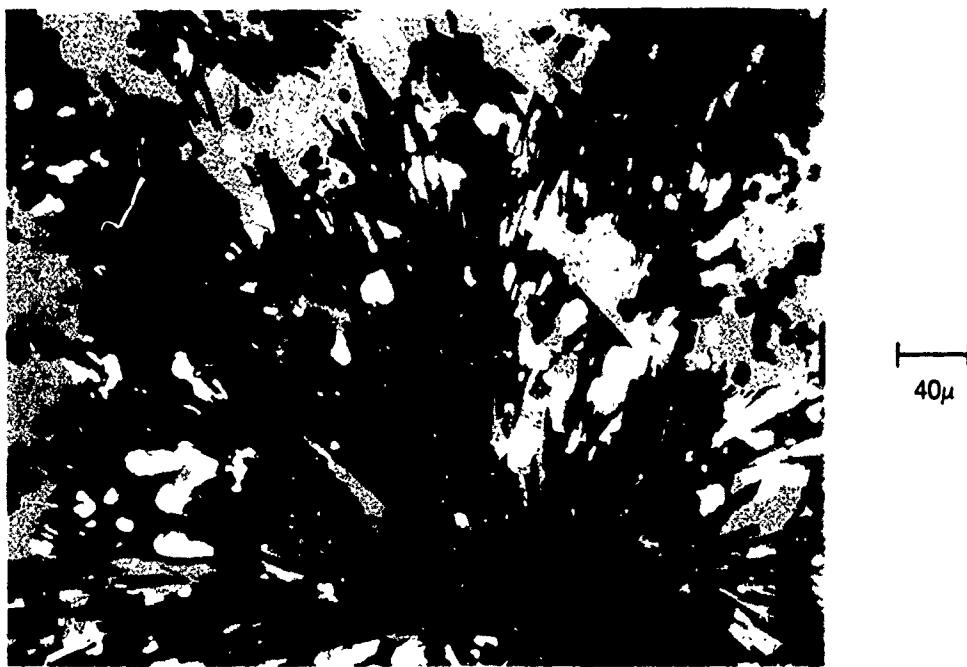


Fig. 9a. Optical micrograph at 250 $\times$ .

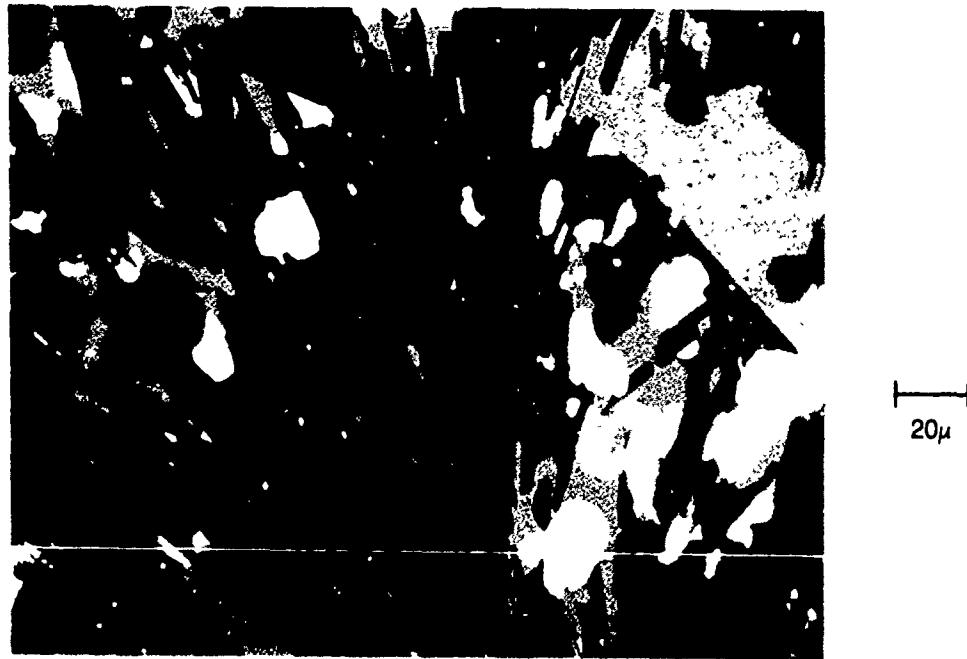
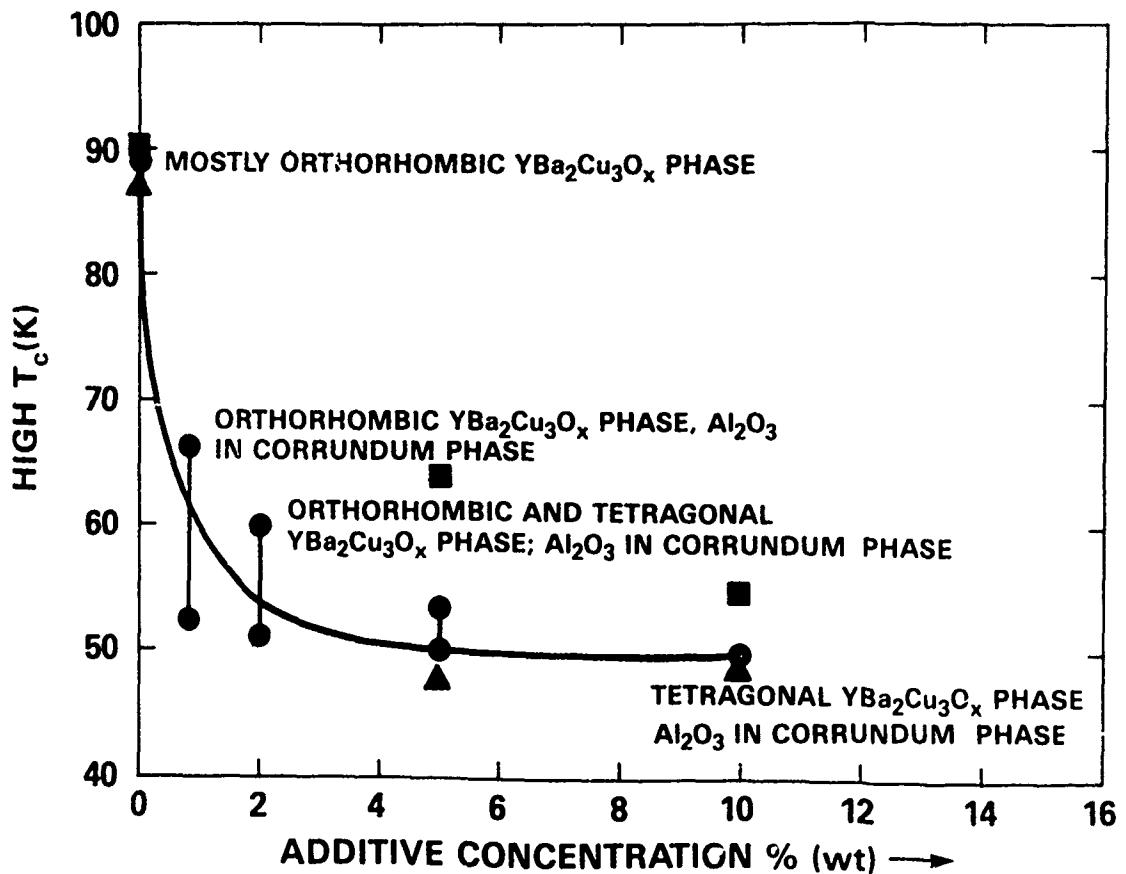


Fig. 9b. Optical micrograph as in a. above except at 500 $\times$ .

Fig. 9. Optical micrographs of  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  superconductor with 15 weight percent added silver oxide.



**Fig. 10.** Superconducting transition temperature versus additive concentration of sintered alumina/(YBaCu) oxide composites. (●) as-sintered and annealed samples, (■) original samples after reannealing in excess flow oxygen and (▲) fresh air.

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